

Two-dimensional carbon allotropes from graphene to graphyne

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Graphene has attracted tremendous interest due to its extraordinary electrical, thermal, and physical properties. The graphynes are widely investigated for their variety of structures and electrical properties. Using the *ab initio* global search approach, we predicted three hexagonal and one tetragonal two-dimensional carbon allotrope: C_{65} -, C_{63} -, C_{31} - and C_{41} -sheets. Graphene, C_{65} -sheet, graphenylene, C_{63} -sheet, and graphyne form a series of graphene-like allotropes from graphene to graphyne. These four new carbon allotropes are metallic and are local minimums in their potential energy surfaces. These two-dimensional carbon allotropes are expected to serve as precursors to build various nanotubes, fullerenes, nanoribbons, and other low-dimensional nanomaterials.

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Introduction

Graphene, a two-dimensional (2D) array of planar hexagonal units (C_6) of sp^2 -hybridized carbon atoms, has attracted tremendous interest due to its extraordinary electrical, thermal, and physical properties.^{1–4} As a 2D building material for carbon materials of all other dimensionalities it can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite.⁵ The success of this building material has motivated much interest in constructing new single-atom-thick periodic carbon networks consisting of different carbon polygons.

Carbon can form a variety of polygons ranging from linear chains to dodecagons with its sp - and/or sp^2 -hybridized atoms. Besides graphene, consisting only of C_6 hexagons, many other 2D periodic carbon allotropes have been predicted and investigated, such as graphynes,^{6–13} graphdiyne,^{14,15} graphenylene,¹⁶ biphenylene,¹⁷ a (3,12)-sheet consisting of triangles and dodecagons,¹⁸ a (4,8)-sheet consisting of squares and octagons,^{18–20} the “benzation” of graphene upon the addition of monovalent atoms (H, F, Cl),²¹ and many carbon allotropes based on the structural defects of graphene.^{22–27} Notably, graphdiyne, a non-natural 2D carbon allotrope, was synthesized in 2010.¹⁴ Therefore, it is interesting to explore the possible 2D carbon allotropes including C_2 , C_3 , C_4 , C_5 , and/or C_6 polygons. In this work, we will focus on the hexagonal and tetragonal 2D carbon allotropes.

A systematic conformational search method is necessary to obtain the possible 2D carbon networks. Recently, we developed an *ab initio* global search approach and successfully found a series of stable 2D boron sheets.²⁸ Using this *ab initio* global

search approach, we will explore some new 2D carbon allotropes and investigate their geometric and electronic properties.

Results and discussion

The *ab initio* global search found several hexagonal and tetragonal carbon allotropes, including the known graphene, graphyne, (3,12)- and (4,8)-sheets. In this work, we do not investigate the (3,12)- and (4,8)-sheets because the planar (3,12)- and (4,8)-sheets have been widely investigated.^{6,18–20} Therefore, we will investigate the geometric and electronic properties of seven 2D carbon allotropes: six hexagonal and one tetragonal one (see Fig. 1 and Table 1).

To confirm their structural stability, the phonon spectra of all of these carbon allotropes were calculated, as shown in Fig. 2. Their phonon dispersion curves demonstrate the absence of any imaginary frequencies, and therefore they are the genuine local minimums on the potential energy surfaces, and capable of existing in reality.

The variety of these carbon allotropes needs them to be named systematically. Because these allotropes can be seen as the network of some C_1 (sp^2 -hybridized carbon atom), C_2 ($C\equiv C$ chain), C_3 , C_4 , C_5 and C_6 polygons, we use the combination of their C_n ($n = 1–6$) structural elements to name them. According to this nomenclature, graphene, graphenylene, and graphyne can be seen as networks of the C_6 hexagons (orange) connected by the C_6 hexagons (blue), C_4 tetragons (blue), and C_2 chains (A, C, E in Fig. 1) so they are named as C_{66} -, C_{64} -, and C_{62} -sheets, respectively.

The two new allotropes, Fig. 1B and D, should be named as C_{65} - and C_{63} -sheets, respectively. In the C_{65} -sheet, the C_6 hexagons are connected by the trefoil C_{10} -units tiled by three C_5 pentagons. In the C_{63} -sheet, the C_3 triangles connect the C_6

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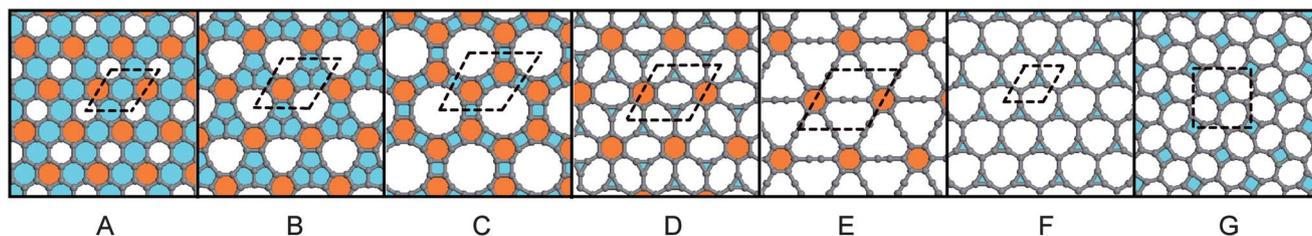


Fig. 1 Geometric structures of the 2D carbon allotropes: C_{66} -, C_{65} -, C_{64} -, C_{63} -, C_{62} -, C_{31} - and C_{41} -sheets from A to G. The orange-filled and blue-filled polygons indicate two different units in the carbon sheets. The dashed tetragons show the unit cells in the carbon sheets.

hexagons by their terminal carbon atoms. As shown in Fig. 1A–E, the C_6 hexagons are connected by C_n polygons ($n = 6-2$) by different patterns. Consequently, the C_{66} -, C_{65} -, C_{64} -, C_{63} -, and C_{62} -sheets form a series of graphene-like allotropes from graphene to graphyne. In this C_{6n} series of graphene-like allotropes, the C_6 , C_5 , and C_4 polygons prefer to connect the C_6 hexagons by fusing their edges in the C_{66} -, C_{65} -, and C_{64} -sheets, while the C_3 triangles and C_2 chains connect with their terminal carbon atoms in the C_{63} -, and C_{62} -sheets, respectively.

There are two other new non-graphene-like allotropes, the C_{31} - and C_{41} -sheets (Fig. 1F and G). The C_{31} - and C_{41} -sheets are the networks of C_3 triangles and C_4 squares connected by the C_1 units, *i.e.* sp^2 -hybridized carbon atoms. Obviously, the sp^2 -hybridized carbon atom can appear as an elementary unit in 2D carbon allotropes to connect the structural polygons. In addition, the C_{41} -sheet is not hexagonal, but tetragonal, which is different to the other 2D carbon allotropes in this work. The C_{41} -sheet is the second most stable 2D tetragonal carbon allotropes after the (4,8)-sheet.

To investigate the stability of these 2D carbon allotropes, we evaluated their relative stable energies $E_s = E_{\text{sheet}} - E_{\text{graphene}}$, where E_{sheet} and E_{graphene} are the energies per atom in a sheet and in graphene using the Perdew–Ernzerhof–Burke (PBE)²⁹ functionals, respectively. Obviously, these four new allotropes are less stable compared to graphene. The C_{65} -, C_{41} - and C_{63} -sheets are 0.231, 0.212, and 0.112 eV more stable per atom than graphyne, and the C_{31} -sheet is only 0.049 eV less stable per atom than graphyne. Therefore, it is possible to synthesize these four new allotropes in experiments.

The electronic properties of these new 2D carbon allotropes are very interesting. Their electronic band structures

and total and partial ($\sigma_{s+p_{xy}}$ and π_{p_z}) density of states are shown in Fig. 3. As seen in Fig. 3 and Table 1, both graphyne and graphenylene are semiconductors with small energy band gaps, 0.460 and 0.034 eV, respectively, which are agreement with the previous results (0.47 eV (ref. 10) and 0.025 eV (ref. 16)), respectively. The four new 2D carbon allotropes have Fermi levels located within the gaps of the in-plane derived partial density of states (PDOS, $\sigma_{s+p_{xy}}$) so that all the σ bonding states are filled, while their σ antibonding ones remain empty. The out-of-plane induced PDOS (π_{p_z}) and therefore the total density of states of these stable carbon allotropes possess non-zero values at their Fermi levels, showing that there are certain occupations in their delocalized out-of-plane induced π -states. Thus, these new four 2D carbon allotropes: C_{65} -, C_{63} -, C_{31} -, and C_{41} -sheets are predicted to be metallic in their p_z -derived bands.

Conclusions

Using the *ab initio* global searches, we found four new 2D carbon allotropes: three hexagonal ones (C_{65} -, C_{63} -, and C_{31} -sheets) and one tetragonal one (C_{41} -sheet). The C_{66} - (graphene), C_{65} -, C_{64} -, C_{63} -, and C_{62} -sheets (graphyne) form a series of graphene-like carbon allotropes from graphene to graphyne. The C_{65} -, C_{63} - and C_{41} -sheets are more stable and the C_{31} -sheet is slightly less stable than graphyne. The electronic band structures and total and partial density of states demonstrated that these four new 2D carbon allotropes are π -metallic. These 2D carbon allotropes are expected to serve as precursors to build various nanotubes, fullerenes, nanoribbons, and other low-dimensional nanomaterials.

Table 1 Component polygons, lattice systems, lattice parameters a (Å), relative stable energies E_s (eV per atom) and energy band gaps E_g (eV) of the 2D carbon allotropes

Name	Common name	Structural polygons	Lattice system	a	E_s	E_g
C_{66}	Graphene	6	Hexagonal	2.468	0.000	0
C_{65}	—	6,5	Hexagonal	5.735	0.407	—
C_{64}	Graphenylene	6,4	Hexagonal	6.766	0.632	0.034
C_{63}	—	6,3	Hexagonal	6.321	0.526	—
C_{62}	Graphyne	6,2	Hexagonal	6.890	0.638	0.460
C_{31}	—	3,1	Hexagonal	3.844	0.687	—
C_{41}	—	4,1	Tetragonal	5.790	0.426	—

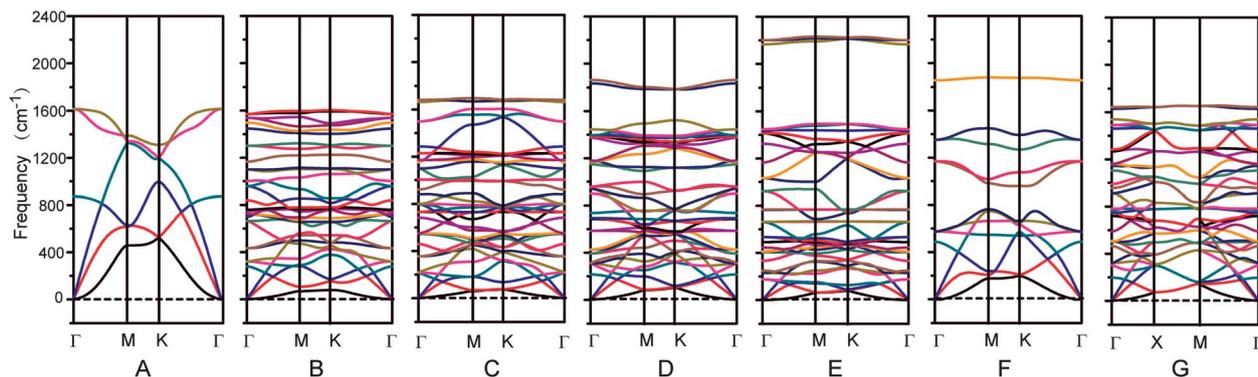


Fig. 2 Phonon dispersion curves along selected directions within the Brillouin zone of 2D carbon allotropes: C₆₆-, C₆₅-, C₆₄-, C₆₃-, C₆₂-, C₃₁- and C₄₁-sheets from A to G.

Computational methods

The global search approach is based on a rectangle (about 40 Å × 40 Å) of the monolayer triangular sheet (with the C–C bond length of $r_{\text{C-C}} = 1.40$ Å). In each possible unit cell of n carbon atoms ($n = 2-25$), its carbon sheets with m holes ($m = 1$ to $n - 1$) were successively yielded according to the procedure in ref. 27. The sheets consisting only of 2- and 3-coordinated carbon atoms (about 660 000) were extracted and their lattice constants and the positions of atoms were optimized using the DFTB+ program^{30,31} with the $3 \times 3 \times 3$ k -points in the Monkhorst–Pack scheme.³² The optimized sheets were symmetrized using the FINDSYM module of the ISOTROPY package³³ to extract the hexagonal and tetragonal allotropes.

The hexagonal and tetragonal sheets were re-optimized by the VASP5.2 package^{34,35} using the projector augmented wave (PAW) method³⁶ in conjunction with the PBE functional and employing a planewave basis set with a 500 eV kinetic energy cutoff. The Brillouin zone is sampled using k -points with

0.02 Å⁻¹ spacing in the Monkhorst–Pack scheme. All carbon sheets are represented by a unit cell with a 20 Å vacuum region in the normal direction. For geometric optimization, both the lattice constants and positions of atoms were fully relaxed. Upon optimization, the forces on all atoms are less than 0.01 eV Å⁻¹ and the criterion for total energy convergence is 0.1 meV per atom.

Phonon calculations were performed by the supercell approach. Real-space force constants of supercells were calculated in the density-functional perturbation theory (DFPT) implemented in the VASP5.2 package, and phonon frequencies were calculated from the force constants using the PHONOPY 1.6.2 code.^{37,38}

Notes and references

- 1 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, V. Dubonos and A. A. Firsov, *Nature*, 2005, **438**, 197.

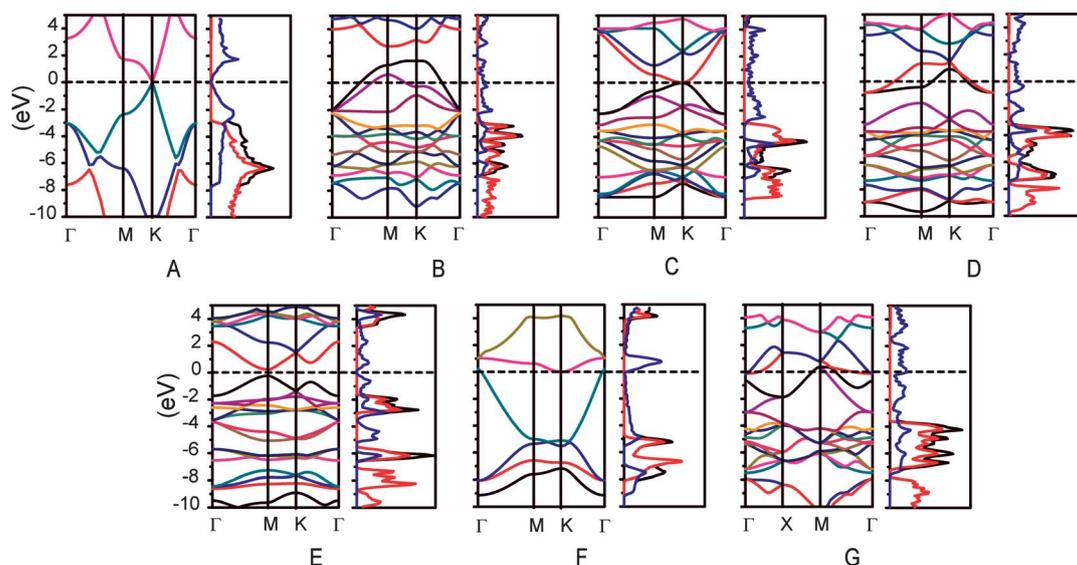


Fig. 3 Calculated electronic band structures (left) and density of states (DOS, right) of the 2D carbon allotropes: C₆₆-, C₆₅-, C₆₄-, C₆₃-, C₆₂-, C₃₁- and C₄₁-sheets from A to G. The Fermi energy (dashed lines) is set as zero. The black, red and blue lines in the right panels indicate the total, σ and π DOS, respectively.

- 2 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666.
- 3 A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, *Nano Lett.*, 2008, **8**, 902.
- 4 C. Lee, X. Wei, J. W. Kysar and J. Hone, *Science*, 2008, **321**, 385.
- 5 A. K. Geim and K. S. Novoselov, *Nat. Mater.*, 2007, **6**, 183.
- 6 A. N. Enyashin and A. L. Ivanovskii, *Phys. Status Solidi B*, 2011, **248**, 1879.
- 7 R. H. Baughman, H. Eckhardt and M. Kertesz, *J. Chem. Phys.*, 1987, **87**, 6687.
- 8 N. Narita, S. Nagai, S. Suzuki and K. Nakao, *Phys. Rev. B: Condens. Matter*, 1998, **58**, 11009.
- 9 V. R. Coluci, S. F. Braga, S. B. Legoas, D. S. Galvao and R. H. Baughman, *Phys. Rev. B: Condens. Matter*, 2003, **68**, 035430.
- 10 J. Zhou, K. Lv, Q. Wang, X. S. Chen, Q. Sun and P. Jena, *J. Chem. Phys.*, 2011, **134**, 174701.
- 11 S. W. Cranford and M. J. Buehler, *Carbon*, 2011, **49**, 4111.
- 12 D. Malko, C. Neiss, F. Vines and A. Gorling, *Phys. Rev. Lett.*, 2012, **108**, 086804.
- 13 B. G. Kim and H. J. Choi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2012, **86**, 115435.
- 14 G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256.
- 15 M. Long, L. Tang, D. Wang, Y. Li and Z. Shuai, *ACS Nano*, 2011, **5**, 2593.
- 16 Q. Song, B. Wang, K. Deng, X. Feng, M. Wagner, J. D. Gale, K. Mullen and L. Zhi, *J. Mater. Chem. C*, 2013, **1**, 38.
- 17 M. A. Hudspeth, B. W. Whitman, V. Barone and J. E. Peralta, *ACS Nano*, 2010, **4**, 4565.
- 18 E. Konstantinova, S. O. Dantas and P. M. V. B. Barone, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 035417.
- 19 J. Nisar, X. Jiang, B. Pathak, J. Zhao, T. W. Kang and R. Ahuja, *Nanotechnology*, 2012, **23**, 385704.
- 20 Y. Liu, G. Wang, Q. Huang, L. Guo and X. Chen, *Phys. Rev. Lett.*, 2012, **108**, 225505.
- 21 I. A. Popov, Y. Li, Z. Chen and A. I. Boldyrev, *Phys. Chem. Chem. Phys.*, 2013, **15**, 6842.
- 22 F. Banhart, J. Kotakoski and A. V. Krasheninnikov, *ACS Nano*, 2011, **5**, 26.
- 23 V. H. Crespi, L. X. Benedict, M. L. Cohen and S. G. Louie, *Phys. Rev. B: Condens. Matter*, 1996, **53**, R13303.
- 24 H. Terrones, M. Terrones, E. Hernandez, N. Grobert, J.-C. Charlier and P. M. Ajayan, *Phys. Rev. Lett.*, 2000, **84**, 1716.
- 25 M. Deza, P. W. Fowler, M. Shtogrin and K. Vietze, *J. Chem. Inf. Model.*, 2000, **40**, 1325.
- 26 J. Lahiri, Y. Lin, P. Bozkurt, I. I. Oleynik and M. Batzill, *Nat. Nanotechnol.*, 2010, **5**, 326.
- 27 G. Brunetto, P. A. S. Autreto, L. D. Machado, B. I. Santos, R. P. B. dos Santos and D. S. Galvao, *J. Phys. Chem. C*, 2012, **116**, 12810.
- 28 H. Lu, Y. Mu, H. Bai, Q. Chen and S.-D. Li, *J. Chem. Phys.*, 2013, **138**, 024701.
- 29 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 30 B. Aradi, B. Hourahine and Th. Frauenheim, *J. Phys. Chem. A*, 2007, **111**, 5678.
- 31 D. Porezag, T. Frauenheim, T. Köhler, G. Seifert and R. Kaschner, *Phys. Rev. B: Condens. Matter*, 1995, **51**, 12947.
- 32 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B: Solid State*, 1976, **13**, 5188.
- 33 H. T. Stokes, D. M. Hatch and B. J. Campbell, *ISOTROPY*, 2007, <http://stokes.byu.edu/isotropy.html>.
- 34 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.
- 35 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter*, 1996, **54**, 11169.
- 36 P. E. Blöchl, *Phys. Rev. B: Condens. Matter*, 1994, **50**, 17953.
- 37 A. Togo, F. Oba and I. Tanaka, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2008, **78**, 134106.
- 38 A. Togo, *Phonopy 1.6.2*, <http://phonopy.sourceforge.net/>.